STUDIES OF POLYMER-FILLER INTERACTIONS IN FILLED SYSTEMS

Alamgir Karim, Kathleen Barnes, Alan Nakatani**, Da-Wei Liu, Jack F. Douglas* and *Eric J. Amis*

Polymers Division, NIST, Gaithersburg, MD 20899
* Presently at Dow Corning, Midland, MI
** Presently at Rohm and Haas Company, Spring House, PA

Introduction

Polymer materials are hardly ever used in their pure form in applications. They are often filled with additives that improve their processibility (lubricants and stabilizers) and filler particles that modify modulus and strength (carbon black, silica, glass beads and fibers, chalk, clay, mica), appearance (pigments and surfactants), conductivity (metal flakes, carbon black, carbon nanotubes), and flammability (flame retardants)[1]. Moreover, a large number of applications necessitate the use of polymer blend materials (impact modified blends, barrier polymers for packaging, filled elastomers) so that the situation where the filler particles interact with the phase separation process is widely encountered. An understanding of polymer-filler interactions and the ramifications for the properties of filled polymer blends is clearly a matter of practical interest that requires further investigation. An understanding of the influence of polymer-surface interactions on the interfacial properties of nanoparticle fillers in polymer matrices is particularly important for applications of nanoparticle filled polymer materials. The influence of nanoparticle-surface interactions is additionally important in understanding and controlling the morphology of coated polymer films containing filler particles. We summarize some of our recent investigations of filler effects on the properties of bulk and polymer film materials.

Results and Discussion

Filler Modification of Blend Phase Stability We investigate the influence of filler particles on the phase stability of a model blend of polystyrene (PS) and polybutadiene (PB). The upper critical solution temperature cloud point curve of PS/PB is "destabilized" (upward shift of cloud point temperature) for fumed silica filler particles (Fig. 1). These phase boundary shifts have significance for morphology and processing of commercial blends containing dispersions of filler particles. Similar shifts in the phase boundary of blend films are observed by adding block copolymer or small molecule additives to a blend mixture [2].

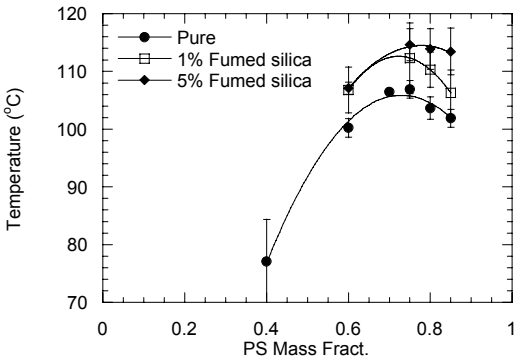

Figure 1. Cloud point curves for the PS:PB blend for unfilled vs. filled fumed silica blends with filler amounts. Bars on data points indicate ± one standard deviation.

Transient Morphology in Phase Separating Filled Blends. Recent simulations suggest that the presence of filler particles in a phase separating blend can induce the development of composition waves having the symmetry of the filler particles. We investigate these predictions through atomic force microscopy (AFM) measurements on ultrathin (L » 100 nm) polystyrene and poly (vinyl methyl) ether blend films containing a low concentration of model filler particles (silica particles having a diameter » 100 nm). The filled blend films were spun cast on acid cleaned silica wafers and phase separation was induced by a temperature jump into the two-phase region (T »145 °C) of the bulk polymer blend. By rinsing off the polymer film with solvent, we show that the silica particles are immobilized on the substrate so that the filler particles represent a quenched disorder perturbation of the film phase separation. The presence of the filler particles leads to the development of circular composition waves ("target patterns") about the filler particles during the intermediate stage of phase separation (Fig. 2) [3]. These target patterns break-up as the background spinodal phase separation pattern becomes much larger than the filler particles. Our observations are consistent with idealized two-dimensional Cahn-Hillard-Cook simulations[4] on the phase separation of polymer blends having a small concentration of filler particles (Fig. 2).

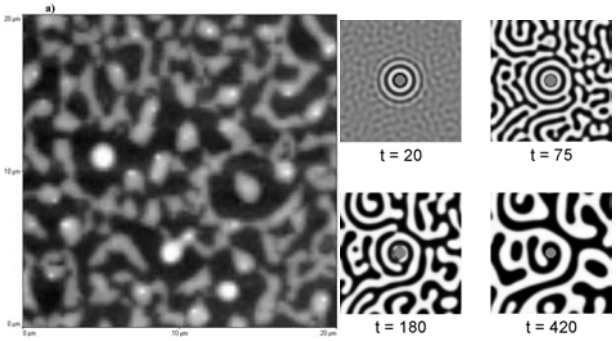

Figure 2. Atomic force microscopy (AFM) image (Image on left) of PS-rich "target" patterns of an intermediate-stage phase-separated PS/PVME blend film containing 100 nm Si particles (Image width = 20 μm). Image sequence on right shows the time development of simulated phase separation pattern in the presence of a filler particle. Time in figure is given in dimensionless units involving the collective diffusion coefficient and the initial scale of the phase separation pattern.

In the absence of fillers the phase separation pattern would form a bicontinuous "spinodal pattern" characteristic of ordinary blend phase separation. "Target" composition patterns are observed about the filler particles in the filled films arising from the symmetry breaking effect of the filler particles. The theoretical modeling indicates that low concentration of filler particles have little influence on the blend morphology in the late stage of phase separation and this effect is found also in our silica bead filled blend films. However, for larger filler size or higher filler concentrations, the late-stage morphology can be pinned by filler particles. Experimentally we find similar pinning effects of late stage morphology by 250 nm size silica bead fillers that are also immobilized on the surface.

Particle Dispersion Effect on Phase Separation Morphology. To gauge the influence of filler particle dispersion on blend morphology we considered a simple experiment in which the fumed silica filler was mixed in a PS/PB blend for various times in the one phase region in a twin screw extruder. The mixture was cooled to induce phase separation in order to determine the influence of the degree of particle dispersion on the phase separation morphology. We first observe (Fig.3) that the scale of the phase separated pattern becomes smaller with an increase in the compounding time in the single phase region. We also observe cluster-like regions rich in filler that become smaller after greater mixing time. These aggregates are very large in undispersed films created through solvent casting of the blend and filler. We interpret our observations in the following way: Initially in the uncompounded state, larger filler aggregates distributed heterogeneously lead to the formation of fractal-like aggregate structures that dominates the phase separation process. We believe the heterogeneity of phase separation induced by the filler is due to a preferential wetting of the filler by one of the blend components. As the silica agglomerates become increasingly broken up (more homogeneous distribution) with an increase of the mixing time, the phase separated morphology become more homogeneous. These results point to the importance of compounding time on blend morphology development and

suggest a regime of "percolation" of wetting layers at high filler concentrations which can possibly dominate the phase separation at long times and over large spatial scales.

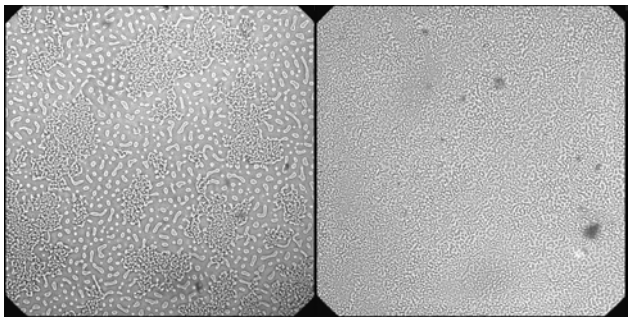

Fig. 3 Optical micrographs of bulk phase-separated PS/PB blend films containing fumed silica (1% filler by mass) compounded in the single phase region for 1 min (left) vs. 10 min (right) at 20x objective magnification. Both films were annealed identically in the two-phase region. Width of image corresponds to 100 mm.

Suppression of Dewetting of Coated Filled Films by Nanofillers The perturbing influence of nanoparticles on the dewetting of spun cast polymer films is investigated[5]. Previous studies have shown that spun cast films of unentangled polystyrene (PS) and polybutadiene (PB) dewet acid-cleaned silicon wafers when the films are annealed above their bulk glass transition temperature Tg and that "impurity" particles tend to promote dewetting in thin films[6]. We observe (Fig.4) that the addition of a small amount of buckminsterfullerene ("fullerene") filler to the spin casting polymer solution leads to a strong suppression of dewetting in thin (L < 100 nm) PS and PB films. Neutron reflection measurements indicate that this effect is associated with the formation of a diffuse fullerene layer near the silicon boundary. Evidently, the immobilized fullerene particles near the solid substrate "pin" the contact line of the growing dewetted ("dry") regions so that hole growth in the filled films becomes arrested at a scale that diminishes with increasing filler concentration. Above a filler mass fraction of 1 % of the total polymer mass in solution we observe a complete suppression of hole formation.

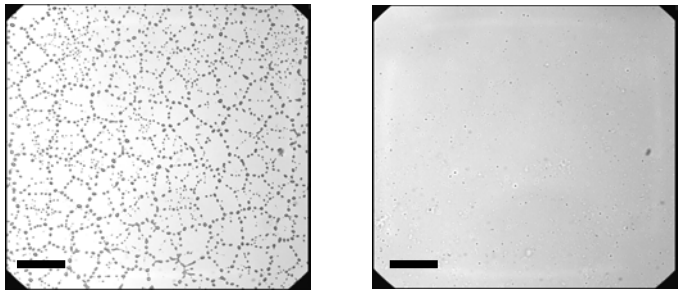

Fig. 4 Optical micrographs showing dewetting of 20 nm PS films annealed at 100 ^{o}C for 30 min (left) vs. another film annealed at 140 ^{o}C for 150 min, containing only 0.005 % bucky balls nanofiller by mass (right). Films were spun cast on acid cleaned silicon wafers (scale bar = 300 μm).

A comparison of our findings with other recent measurements suggest that the pinning occurs very differently when the filler is immobilized by the substrate as in our study (quenched disorder) than when the filler freely moves within the polymer film (annealed disorder).

Conclusions

We observe that the presence of filler particles can have a major impact on the properties of filled polymer blend materials. The filler particles, which are found in many commercial polymer blends, modify the phase boundary (interfacial tension, rate of phase separation), the geometrical form of the phase separation morphology, the transport properties of the filled polymer material, the stability of polymer films against dewetting.

Disclaimer. Certain commercial materials and instruments are identified to adequately specify the experimental procedure. This does not imply recommendation or endorsement by NIST nor does it imply that materials or equipment identified are necessarily the best available for the purpose.

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References

(1) Meijer, H.E.H.; Lemstra, P.J.; Elemans, P.H.M. *Makromol. Chem., Makromol. Symp*. **1988,** *16*, 113.
(2) A. Karim, D.W. Liu, J.F. Douglas, A.I. Nakatani, E.J. Amis, *Polymer* **1999**, *41,*8455; J. Dudowicz, K.F. Freed, J.F. Douglas, *Macromolecules*, **1995**, *28*, 2276.
(3) A. Karim, J.F. Douglas, G. Nisato, D.W. Liu, E.J. Amis, *Macromolecules*, **1999**, *32*, 5917.
(4) B.P. Lee, J.F. Douglas, S.C. Glotzer, *Phys. Rev. E*, **1999**, *60*, 5812.
(5) K.A. Barnes, A. Karim, J.F. Douglas, A.I. Nakatani, H. Gruell, E.J. Amis, *Macromolecules*, **2000**, *33*, 4177.
(6) See for example, Reiter, G., Phys. Rev. Lett., **1992**, *68*, 75; R. Xie, A. Karim, J.F. Douglas, C.C. Han, R.A. Weiss, Phys. Rev. Lett., **1998**, *81*, 1251.